Statistical investigations of basis weight and thickness distribution of continuously produced fuel cell electrodes

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HIGHLIGHTS

- The knife coating process for electrode production is investigated.
- Investigation of electrode basis weight distribution indicates coating defects.
- A construction fault in the coating machine causes a gradient in the catalyst layer.
- Variance of catalyst basis weight is determined by properties of the substrate used.

ARTICLE INFO

ABSTRACT

The presented work is focused on the investigation of catalyst basis weight scattering in direct methanol fuel cell electrodes produced by a roll-to-roll process. For the manufacturing of highly efficient electrodes the statistical variance of the catalyst basis weight should be as small as possible.

The dependencies between the variances of the catalyst basis weight, substrate basis weight, substrate thickness, and electrode basis weight are inferred from theoretical considerations. A commercial substrate is coated with catalyst dispersion by a continuous knife coating process to manufacture the electrodes. The basis weight and thickness of the substrate and the electrode are investigated ex-situ. The distribution of the measurands enables the determination of an estimator for the expected value and the variance which are used to calculate the variance of the catalyst basis weight.

The main finding of the investigations is that different impacts on the distribution of the catalyst basis weight exist. A construction fault in the coating knife of the employed coating machine causes a gradient in the catalyst layer. After removing this fault it can be proved that a periodic structure in the substrate basis weight and thickness is responsible for a large contribution to the catalyst basis weight variance.

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1. Introduction

Over the last few years, a number of direct methanol fuel cell (DMFC) prototype systems have been developed [1,2]. They are interesting for many applications, such as battery replacement in mobile electronic, fork lifts, or uninterruptible power supplies [3,4]. Though some systems fulfill the requirements of longevity they are still very expensive in comparison to well-established systems, such as battery systems [5]. One strategy to reduce the investment and operating costs of fuel cell systems is to increase the electrical efficiency.

The efficiency of a DMFC system is primarily determined by the membrane electrode assemblies (MEAs). They must be able to convert the chemical energy of methanol to electrical energy with maximum efficiency, maximum power density, and with as little expensive catalyst as possible. To achieve these apparently conflicting requirements, it becomes necessary to find appropriate production processes and materials for the manufacturing of the electrodes which are important subcomponents of the MEA.

The processes and materials are generally tested and developed in laboratory scale [6,7]. Small amounts of material and laboratory equipment are used for the discontinuous production of test electrodes to investigate physical and electrochemical correlations. If appropriate processes and materials are identified, the processes must be scaled up for the pilot plant production. For this scale-up it is essential that the large-sized electrodes have uniform physical properties over the entire active area.

One important electrode property is the catalyst basis weight. The higher the catalyst basis weight the higher the cell voltage, and gradients in cell voltage are able to affect the electrode efficiency

[8]. Some research has been done to find the optimal catalyst distribution in a catalyst layer [9–11] without considering the fact that every production process generates an undesired distribution with a specific variance. The homogeneity of the catalyst basis weight is of particular attention for the production of large-sized fuel cell electrodes.

The characterization methods for large-sized electrodes can be classified as in-situ and ex-situ methods. The industrial production of uniform stack electrodes requires in-situ methods to control substrate and electrode properties during the production [12]. The main emphasis of this study is research and development of the production processes. In this case, ex-situ methods are more suitable because existing measurement devices can be further developed in an easier way than on-line measurement devices in a production machine.

One core task of the presented work is the manufacturing of homogeneous square meter sized electrodes for direct methanol fuel cells. The electrodes are produced by using a knife coating process for the direct coating of gas diffusion layers with catalyst dispersion. One advantage of this process is the option to produce either small or large electrodes which is important for research and development. Another advantage is the scalability from laboratory to pilot plant scale which is a crucial aspect for the production of large-sized electrodes.

A challenge of the direct coating of dispersions on a porous substrate is the complex interdependency between the substrate and the dispersion. The substrate properties, such as thickness, wetting behavior, and pore size distribution have a direct influence on the structure of the coated layer. Effects like dispersion penetration in the substrate, which is also affected by the rheological properties of the dispersion, can lead to a reduced quality of the electrode. More fundamental research is necessary to understand the complex interdependencies between a porous substrate and a non-Newtonian dispersion.

With regard to the variance of the catalyst basis weight of continuously manufactured electrodes no measured data can be found in literature. Additionally, no systematic investigations of the basis weight or thicknesses distribution of substrates are available. Therefore, the basis weight and thickness distribution of the commercial substrate used and the produced electrodes are statistically analyzed by using an ex-situ method.

The aim of the presented work is the manufacturing of uniform electrodes, the determination of estimators for the statistical expected value and for the variance of the catalyst basis weight. In relation to these estimators the produced electrodes are judged, and different influences between the electrode production process and the variance of the catalyst basis weight are investigated. The challenge is to decrease the variance of the catalyst basis weight in order to increase the electrode efficiency.

2. Experimental

The following sections present a survey about the applied production and investigation techniques in this work. The different challenges are explained, and the relevant equations for the calculation of the catalyst basis weight variance are introduced.

2.1. Electrode production

The first step in electrode production is the in-house preparation of catalyst dispersion with specific catalyst content in the solid phase (ω_{cat}). The dispersion is coated on a substrate by using a knife coating process [13]. After the coating is applied, the electrode is dried, and the mass can be measured to determine the electrode basis weight. For the determination of the electrode catalyst loading the basis weight of the substrate is needed. The calculation

of the catalyst basis weight for a discontinuously produced laboratory electrode is different in comparison with a continuously manufactured pilot plant electrode. This difference is described in the following sections.

2.1.1. Discontinuous electrode production in laboratory scale

For the electrode production in laboratory scale a sample of the substrate is cut out from a substrate roll with the size of the needed electrode. The mass (m_s) and the area (A) of the sample are measured, and the basis weight of the substrate (bw_s) is calculated. In laboratory experiments electrodes with an area of 4.2 cm × 4.2 cm are used. The basis weights of these small samples can be determined very precisely before the coating.

With the assistance of a mask the sample is coated with the catalyst dispersion by a lab coater. After drying, the mass of the electrode (m_e) is measured, and the basis weight of the electrode (bw_e) is determined. Fig. 1 shows the different steps for electrode production in laboratory scale.

The catalyst mass fraction (ω_{cat}) in the solid content of the dispersion is a function of the dispersion composition, and it is needed to calculate the catalyst basis weight of the electrode.

$$bw_{cat} = \omega_{cat} \times (bw_e - bw_s) \tag{1}$$

In case an unknown substrate or a new dispersion is used for the electrode production, laboratory preliminary tests have to answer the question whether or not the substrate can be coated with the dispersion or which adjustments for the coating process are necessary. Furthermore, rheological investigations of the dispersion can help to detect coating problems in advance before the electrodes are produced with the pilot plant.

Currently, the results from laboratory experiments are not fully transferable to the pilot plant production. For example, the catalyst basis weight of a produced laboratory electrode and a pilot plant electrode can be different, even though the same parameter values are used for the manufacturing. Therefore, to produce an electrode with a specific desired catalyst loading, the right adjustment of the knife height (kh, see Section 2.1.3) must be determined in the pilot plant by a calibration experiment. This experiment is described in Section 3.2.

2.1.2. Continuous production of stack electrodes in pilot plant scale

For the manufacturing of stack electrodes with a pilot plant the substrate is initially unrolled from a roll. Afterward, the electrode is
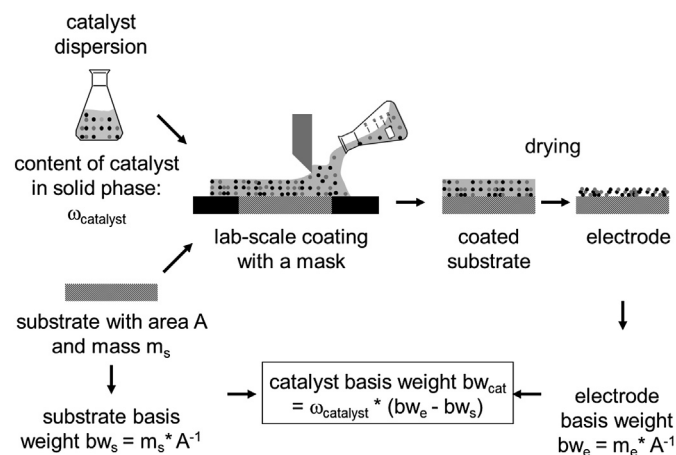

Fig. 1. Schematic representation of the electrode production in laboratory scale. The basis weight of the coated substrate is determined before the coating, and together with the basis weight of the electrode the catalyst loading can be calculated.

coated with the catalyst dispersion by a knife-over-roll coating process. The coated substrate is dried by an air dryer at 80 °C, and at the end of the production the electrode is coiled up. Fig. 2 shows a simplified illustration of the employed production sequence.

The stack electrode's geometry can be punched out from the electrode roll. In comparison to the laboratory production of electrodes the basis weight of the substrate cannot be determined before the coating.

It is known from laboratory investigations that the basis weight of the substrate fluctuates around an average value. The idea for the determination of the catalyst basis weight of the produced electrode roll is to analyze the basis weight distribution of a representative piece of substrate and of a representative piece of electrode. If the mean and the variance of the distributions can be quantified, the mean of the catalyst basis weight distribution can be calculated. Additionally, the variance of the distribution can be determined by the law of error propagation. With the variance, as a measure for the width of the distribution, it is possible to judge the quality of the coating. These steps will be explained in Section 2.3.

2.1.3. Influencing variables on the electrode basis weight

In comparison to other coating processes the knife coating process allows the operator to control the shear forces which influences the catalyst dispersion during the coating process. It is therefore possible to reduce the influence of the coating process on the dispersion and keep the dispersion structure. This is an important aspect because a fuel cell electrode, which has to fulfill many requirements, needs a high level of structure to achieve a high efficiency.

A major disadvantage of the knife coating process results from the interaction between the non-Newtonian catalyst dispersion and the porous substrate. Fig. 3 shows a simplified illustration about a knife coating process. One important parameter for the catalyst basis weight is the distance between the knife and the substrate, the coating thickness (t_c). For the presented work the coating machine used allows only the adjustment of the knife height (kh). Consequently, every local change in the substrate thickness (t_s) changes the coating thickness and influences the wet film thickness (wt). Hence, the basis weight of the electrode is correlated with the substrate thickness.

In the case the substrate thickness is correlated with the substrate basis weight, the basis weight of the electrode will be correlated with the substrate basis weight. From the perspective of a statistician the value of the covariance between the substrate and
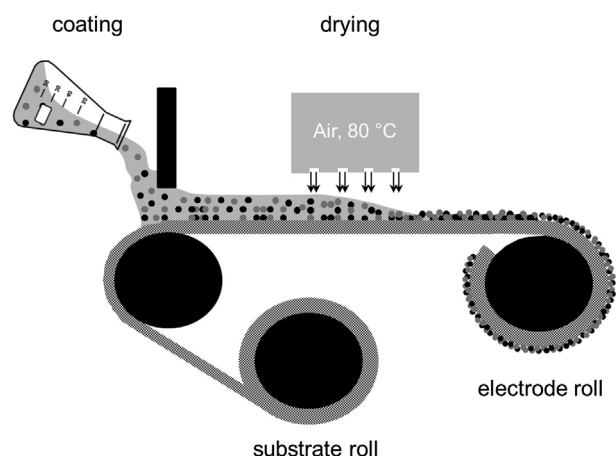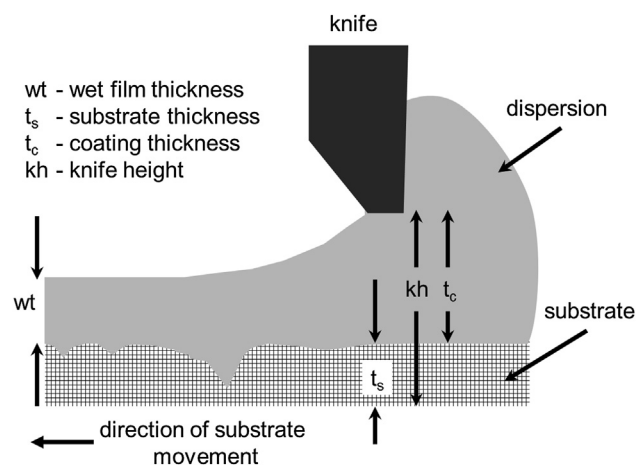

Fig. 3. Schematic illustration of the knife coating process.

electrode basis weight is not zero. This dependency will be important for Section 2.3.

In additional to the discussed relations, every inhomogeneity of the surface property, like porosity or wettability, can cause a penetration of catalyst dispersion in the substrate and therefore an increase of catalyst basis weight.

As a consequence, the homogeneity of the catalyst basis weight is limited by the homogeneity of the substrate. Another limitation of the achievable uniformity is the drying process of the wet film. The transport of momentum by the hot air and capillary transport during the drying are able to cause an inhomogeneity of the basis weight.

The investigation of the statistical distribution of basis weight and thickness of the dried electrode can help to identify the most interfering processes during the electrode production. With this information it is possible to eliminate effects and to increase the homogeneity of electrode properties.

2.2. Statistical distribution of basis weights and thicknesses

To analyze the statistical distribution of substrate and electrode properties, samples in the size of the roll width and one meter length are cut into small samples. The roll width varies between 30 cm for electrodes and 35 cm for the analyzed substrates. To punch out the small samples, a hand-lever press (type: 56kNHKP, Gechter GmbH) is used in combination with a chessboard-like stamping tool (Marbach) with the geometric dimension for the samples of 4.2 cm width and 4.2 cm length. The area of every sample is $A = 17.6$ cm^2. The standard deviation of the punched-out areas is 0.1 cm^2.

2.2.1. Determination of the basis weights

The mass of the punched-out samples is measured by an analytical balance (AT201, Mettler Toledo). Because of the porosity of the samples the mass is influenced by fluctuations in residual moisture. Furthermore, during the stamping process it is possible to lose small particles and fibers of the sample which affects the accurate determination of the mass. These uncertainties are estimated with a standard deviation of 1 mg.

The basis weight is determined by dividing the sample mass by the sample area (Eq. (2)), and the standard deviation is calculated by Gaussian error propagation (Eq. (3)).

$$bw_i = m_i \times A^{-1} \tag{2}$$

$$stdv(bw_i) = sqrt((stdv(m_i) \times A^{-1})^2 + (m_i \times stdv(A) \times A^{-2})^2) \tag{3}$$

Fig. 2. Illustration of the production sequence for a continuous pilot plant electrode production.

2.2.2. Determination of the sample thickness

The thickness of the sample is measured with the thickness gauge DM2010 (Wolf). The applied contact pressure is 160 kPa. The data represents the average of five measured points, four at each corner and one in the middle of the sample. The accuracy of the thickness gauge is 4 µm.

2.2.3. Determination of the stress–strain characteristic

The thickness gauge compresses the sample during the measurement. To guarantee that this compression is reproducible and the measurement is in the elastic range of the sample, a cyclic stress–strain curve of a few samples is measured. A rheometer with a normal stress sensor (MARS III, Thermo Scientific) is used for this investigation. During the measurement the sample is periodically compressed two times from 0 kPa to 180 kPa.

2.2.4. Test on normal distribution

Statistical distributions can be characterized by their statistical moments [14]. These moments cannot be measured, but it is possible to find estimators. The presented work is focused on the scattering of the catalyst basis weight and not on the precise characterization of the measured distributions. Therefore, only the first two moments of the investigated distributions are considered.

For the first moment, the expected value, the average is used as an unbiased estimator. For the second moment, the variance, the square of the standard deviation is used. In the case of a normally distributed variable these two parameters completely characterize the distribution. To decide whether or not the investigated variable is normally distributed, Yazici and Yolacan [15] analyzed different kinds of statistical tests. In case the type of the distribution is initially unknown, they recommend the Jarque–Bera test.

In this work the Jarque–Bera test of the free software R is used (package: tseries, function jarque.bera.test). The test provides a p-value which describes the probability to obtain the measured data assuming that the hypothesis "The measured distribution is normally distributed" is true. A significance level alpha has to be defined. For this work a level of 5% is chosen. If the p-value is less than alpha, the hypothesis above is rejected. More information about statistical tests is available in Ref. [16].

The approach in this work is to measure the thickness and the basis weight and to represent the data as a frequency distribution with the calculated arithmetic average, the standard deviation, and the p-value of the Jarque–Bera test. The p-value is used as an indicator for effects or trends in the investigated samples which disturb the normal distribution.

2.3. Estimation of the mean and variance of the catalyst basis weight distribution

Eq. (1) shows how to calculate the catalyst basis weight of a laboratory electrode when the basis weight of the substrate and the electrode are known. For the electrode roll, produced with the pilot plant, the local basis weight of the substrate is unknown. Therefore, Eq. (1) cannot be used to determine the catalyst basis weight of continuously manufactured electrodes.

The basis weight of the substrate and the electrode are random variables because the values fluctuate over the range of square meters. As a consequence, the catalyst basis weight is a function of the two random variables bw_s and bw_e. Therefore, it will also be a random variable.

According to Papoulis [17], the mean ($E(bw_{cat})$) and the variance ($var(bw_{cat})$) of a function

$$bw_{cat} = bw_{cat}(bw_s, bw_e) = \omega_{cat} \times (bw_e - bw_s)$$

can be estimated in terms of the mean, the variances, and the covariance of bw_s and bw_e as described below:

$$E(bw_{cat}) \approx \omega_{cat} \times (E(bw_e) - E(bw_s)) \tag{4}$$

$$var(bw_{cat}) \approx (\omega_{cat})^2 \times (var(bw_s) + var(bw_e) - 2 \times cov(bw_s, bw_e)) \tag{5}$$

When the basis weight distribution of a representative substrate and electrode sample are known, it is possible to find estimators for the expected value as well as the variance of the substrate and the electrode basis weight. Using these values, the expected value of the catalyst basis weight (Eq. (4)) can be calculated.

Eq. (5) contains the covariance of bw_s and bw_e. This value is a nonzero number in case of a correlation between these two basis weights. According to the explanations in Section 2.1.3, such a correlation exists when the basis weight and the thickness of the substrate are correlated.

To find an experimental estimator for this covariance, the basis weight and thickness of the substrate are investigated. In the presented work the measured data are used to describe the substrate basis weight as a linear function of the thickness. In the case of small variances in the substrate thickness this approach is reasonable because the Taylor series of the function exists. The first and second term of this series can be used as an approximation for the linear function (Taylor approximation).

$$bw_s = ks_0 + ks_1 \times t_s \tag{6}$$

Additionally, the dependency between the electrode basis weight and the coating thickness (t_c, see Fig. 3) is investigated in this work (see Section 3.2). For small variations of the coating thickness the electrode basis weight can be described as a linear function of the coating thickness.

$$bw_e = ke_0 + ke_1 \times t_c \tag{7}$$

Eqs. (6) and (7) in combination with the linearity of the covariance enable the determination of an estimator for the covariance between the electrode and substrate basis weight.

$$\begin{aligned}
cov(bw_e, bw_s) &= cov(ke_0 + ke_1 \times t_c, ks_0 + ks_1 \times t_s) \\
&= cov(ke_0, ks_0) + cov(ke_0, ks_1 \times t_s) \\
&\quad + cov(ke_1 \times t_c, ks_0) + cov(ke_1 \times t_c, ks_1 \times t_s)
\end{aligned} \tag{8}$$

The first, the second, and the third term are zero because there is no existing correlation between the constants of the different linear functions of Eqs. (6) and (7). Therefore it follows:

$$\begin{aligned}
cov(bw_e, bw_s) &= ke_1 \times ks_1 \times cov(t_c, t_s) \quad ; kh = t_s + t_c \rightarrow t_c = kh - t_s \\
&= ke_1 \times ks_1 \times (cov(kh, t_s) - cov(t_s, t_s)) \\
&= -ke_1 \times ks_1 \times cov(t_s, t_s) \\
&= -ke_1 \times ks_1 \times var(t_s)
\end{aligned} \tag{9}$$

The combination of Eqs. (9) and (5) gives the variance of the catalyst basis weight.

$$var(bw_{cat}) = (\omega_{cat})^2 \times (var(bw_s) + var(bw_e) + 2 \times ks_1 \times ke_1 \times var(t_s)) \tag{10}$$

Eqs. (4) and (10) are used to determine the catalyst basis weight and its variance for the produced electrodes. The following sections present the measured data and evaluations.
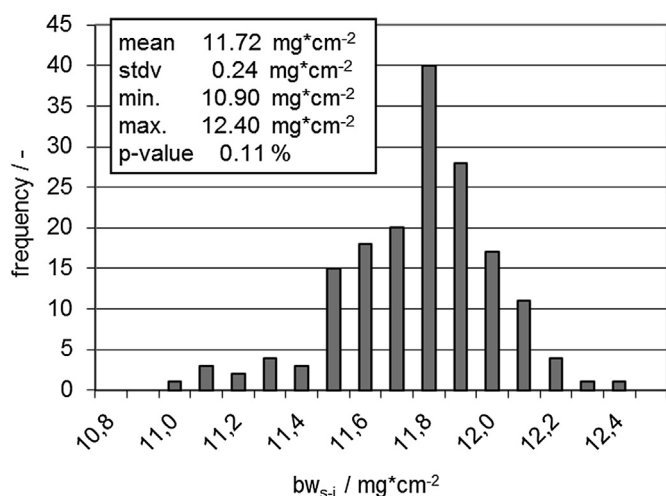
Fig. 4. Frequency distribution of substrate basis weight (type: s–i).

3. Results and discussion

For the coating of a commercial substrate with an in-house produced catalyst dispersion the substrate basis weight and thickness are analyzed in Section 3.1 according to Section 2.2. These investigations provide estimators for the mean and the variance of the distributions and contribute information about the correlation between thickness and basis weight which is important for the determination of the variance of the catalyst basis weight, described in Section 2.3.

In Section 3.2 the dependency between the knife height of the coating unit and the electrode basis weight are investigated. On the basis of this data the needed knife height for the production of an electrode can be determined.

The prescribed catalyst basis weight is 3.2 mg cm^{-2} with a standard deviation of 0.05 mg cm^{-2}. The produced electrodes are judged in relation to the variance of the catalyst basis weight.

3.1. Investigation of the substrate

For the production of electrodes a commercial, non-woven substrate without a microporous layer is used. The manufacturer offers this substrate in a non-impregnated type (labeled in this work with "s") and an impregnated type (labeled in this work with "s–i"). For this study the s–i type is used as a substrate for the coating process.

3.1.1. Basis weight distribution of substrate s–i

A 0.35 m wide and 1 m long substrate is analyzed according to Section 2.2. Fig. 4 shows the frequency distribution of the determined basis weights of all samples tested.

The Jarque–Bera test provides a p-value of 0.1% for the basis weight distribution. This value is smaller than the selected level of significance of 5% (see Section 2.2.4). Therefore, a normally distributed basis weight can be precluded. Fig. 5 presents the substrate basis weight in a contour plot as a function of substrate length and width. At one side of the substrate there is a periodic change in the value of the basis weight from approximately 11.2 mg cm^{-2} to 11.9 mg cm^{-2} with a periodic distance of approximately 25 cm–30 cm in longitudinal direction.

Fig. 4 shows that the measured basis weights between the interval 10.9 mg cm^{-2} and 11.4 mg cm^{-2} increase the width of the frequency distribution. To see the periodicity more clearly, the mean and the standard deviation (stdv) are calculated for each column and for each row of samples, marked in Fig. 5 with (A) and (B). The mean and the standard deviation, calculated for each column, as a function of the substrate length are shown in Fig. 6A. Fig. 6B shows the mean and the standard deviation, calculated for each row, as a function of the substrate width. This kind of data presentation is useful to localize the areas in the substrate that make the greatest contribution to the standard deviation.

Fig. 6A for example shows a periodic increase of the standard deviation from 0.15 mg cm^{-2} up to 0.40 mg cm^{-2}. Furthermore, Fig. 6B indicates that the highest values of the standard deviation occur at a substrate width between 30 cm and 34 cm. The maxima of the standard deviation in Figs. 6A and B show that the periodic minima of the basis weight in the range of 11.20 mg cm^{-2}– 11.60 mg cm^{-2} in Fig. 5 lead to a periodic increase of the standard deviation along the substrate length. This periodic structure increases the standard deviation from 0.11 mg cm^{-2} to 0.30 mg cm^{-2} in the upper region of the substrate (width higher than 17 cm, see Fig. 6B).

On the basis of the presented data it can first noted that a large part of the standard deviation of the substrate basis weight is caused by the measured periodic structure. To get an idea about the source of this structure, the commercially available non-impregnated substrate s is also investigated. According to the manufacturer, the difference between the substrates s and s–i is only the impregnation. The next section shows the result of this investigation.

3.1.2. Basis weight distribution of substrate (s)

The measured basis weight data of substrate s is used for a Jarque–Bera test. Because of a p-value of 0.6% a normal distribution
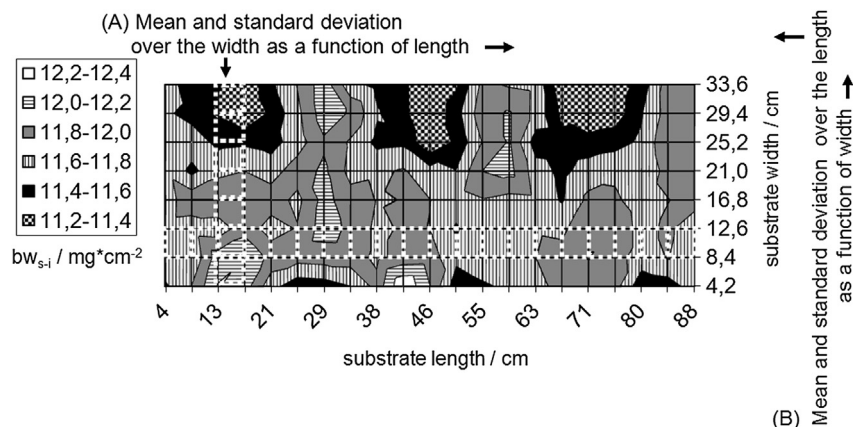

Fig. 5. Contour plot of substrate basis weight (type: s–i) as a function of substrate length and width.

can be precluded. Fig. 7 shows the frequency distribution of the measured basis weights. Additionally, Fig. 8 presents the data in a surface plot. The diagrams show that the basis weight distribution of substrate s has a bimodal structure.

The first local maximum in the frequency distribution of substrate s (see Fig. 7) between 9.2 mg cm^{-2} and 9.6 mg cm^{-2} is created by the base of the surface in Fig. 8. The second local maximum between 9.7 mg cm^{-2} and 10.2 mg cm^{-2} is created by the peaks in Fig. 8. The periodic length of the peaks is approximately 25 cm–30 cm and is very similar to the observed periodic structure discussed in Section 3.1.1.

The presented data in this section gives rise to suspicion that the source of the periodic structure in the substrate basis weight is related to the manufacturing process of the substrate. The periodic structure is responsible for the bimodal distribution and it affects the structure of the basis weight of substrate $s-i$. The next section is related to the investigation of the thickness distribution of substrate $s-i$.

3.1.3. Distribution of the substrate thickness (s−i)

According to the Jarque–Bera test of the substrate thickness data, a p-value of 42% is found, thus a normal distribution of the thickness data cannot be ruled out. Fig. 9 shows the frequency distribution of the substrate thickness, and Fig. 10 shows the same data in a contour plot. In this case the contour plot provides indications of not normally distributed data because of the same periodic structure in comparison to the basis weight, described in Section 3.1.1.

Additionally, Fig. 11 shows the thickness data in a three-dimensional surface plot where the gradients are easier to perceive. The substrate thickness has a periodic structure with a periodic length between 25 cm and 30 cm. This periodic structure is overlaid by a shift from one edge of the substrate to the other. The difference of the thickness between the two edges is approximately 20 μm. Because of these effects a normal distribution of the substrate thickness cannot be assumed. However, the diagrams show that the mean can be used as an estimator for the average thickness and the standard deviation as an estimator for the scattering of the thickness.

At this point it is important to note that the contact method for the thickness measurement has a disadvantage because during the measurement a constant stress compresses the sample. If the thickness is constant but the modulus of elasticity is inhomogeneous, the result of the measurement is an apparent inhomogeneous thickness distribution. To distinguish whether the thickness or the elastic modulus of the substrate varies, a cyclic stress–strain characteristic is measured for two samples with maximum
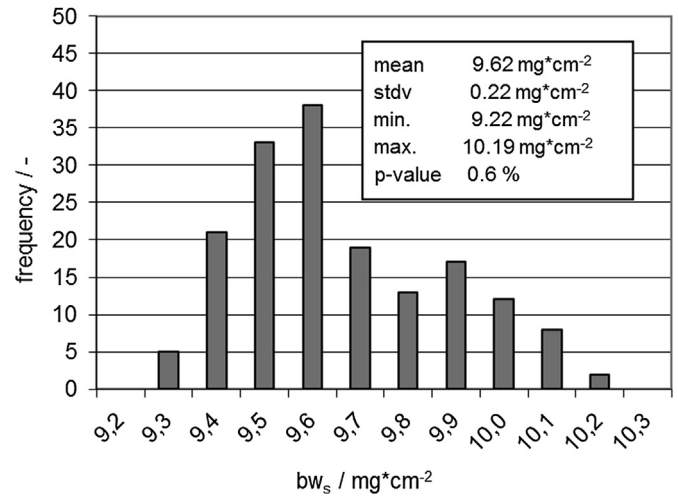
Fig. 7. Frequency distribution of substrate basis weight (type: s).
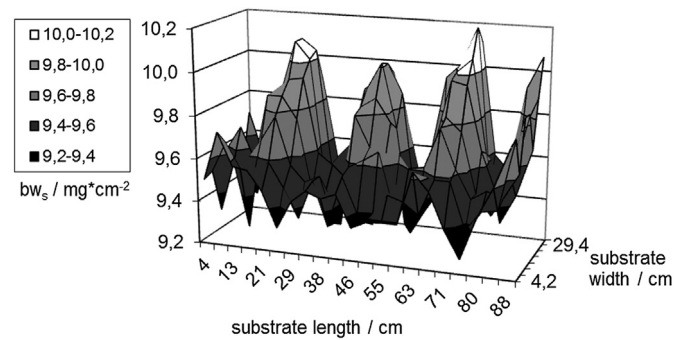
Fig. 8. Surface plot of basis weight for all samples of substrate s as a function of substrate length and width.

difference in the measured thickness. The measured thickness of sample A is 183 μm ± 4 μm and of sample B is 201 μm ± 4 μm.

Fig. 12 shows the measured stress as a function of the sample thickness. The abscissa of a stress–strain curve usually contains the relative deformation, but in the case of the investigated soft substrate it is quite difficult to define an absolute substrate thickness without to deform the sample. The stress–strain characteristics of the two samples show only a horizontal shift and not a difference between the slopes of the curves. Additionally, in comparison with the results from the thickness gauge the curves show, within the
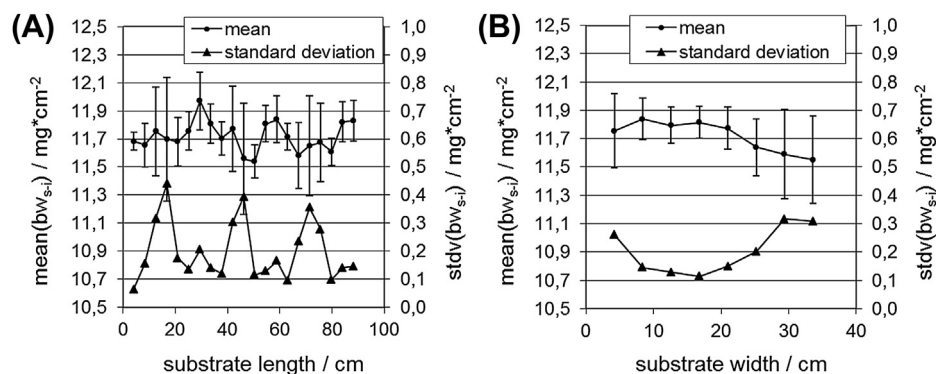
Fig. 6. Mean and standard deviation of substrate basis weight (type: $s-i$). A: Mean and standard deviation over the width as a function of length. B: Mean and standard deviation over the length as a function of width.
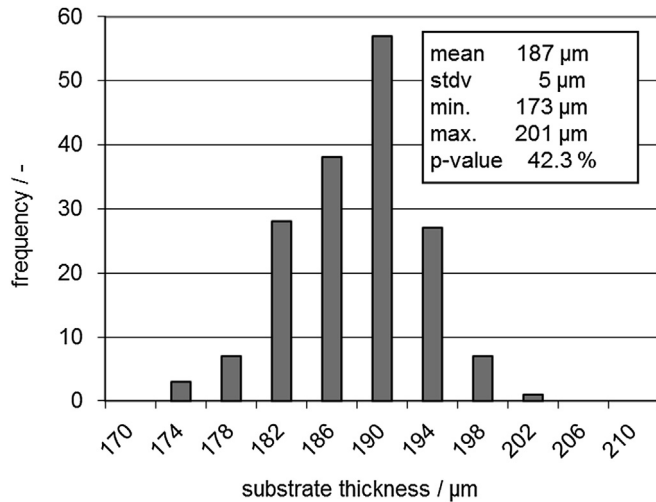
Fig. 9. Frequency distribution of substrate thickness (type: *s—i*).

Fig. 11. Surface plot of substrate thickness for all samples of substrate (type: *s—i*) as a function of substrate length and width.

uncertainties, the same values for the thicknesses at a stress value of 160 kPa. It can therefore be assumed that the measured differences in Fig. 11 are thickness differences of the samples.

In relation to the entire substrate thickness the relative standard deviation of the thickness is approximately 2.6% (5 μm/187 μm). However, as mentioned in Section 2.1.3, it must be assumed that the regions of the substrate with a lower thickness will be filled with dispersion during the coating process. This may have a strong effect on the homogeneity of the catalyst distribution especially in case of thin catalyst layers on the substrate.

A final assessment of the described structures in the substrate thickness will be made together with the catalyst basis weight distribution data in Section 3.5.2. The next section considers the correlation between the substrate basis weight and the thickness which is important for the calculation of the variance in the catalyst basis weight, described in Section 2.3.

3.1.4. Basis weight − thickness correlation of substrate s−i

According to Section 2.3, we assume a linear dependency between the basis weight and thickness of the substrate in order to calculate the covariance between the electrode and substrate basis weight. This assumption is reasonable because a Taylor series of the function $bw_s(t_s)$ always exists, and in case of small variations in the thickness the first and the second term of this series can be used as an approximation.

Fig. 13 shows the basis weight as a function of the thickness for each sample. In this plot the periodic structure in the substrate, discussed in Sections 3.1.1 and 3.1.3, is responsible for the
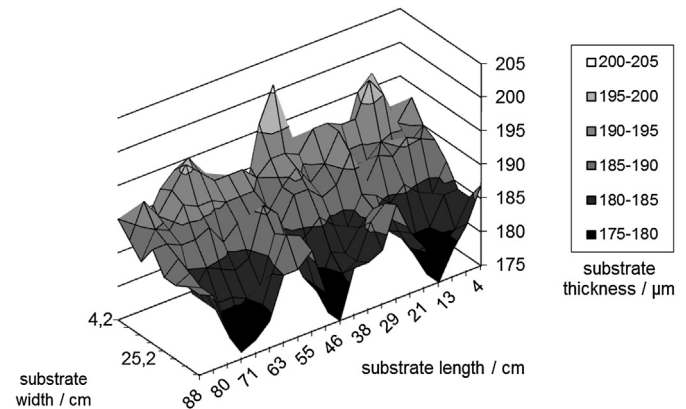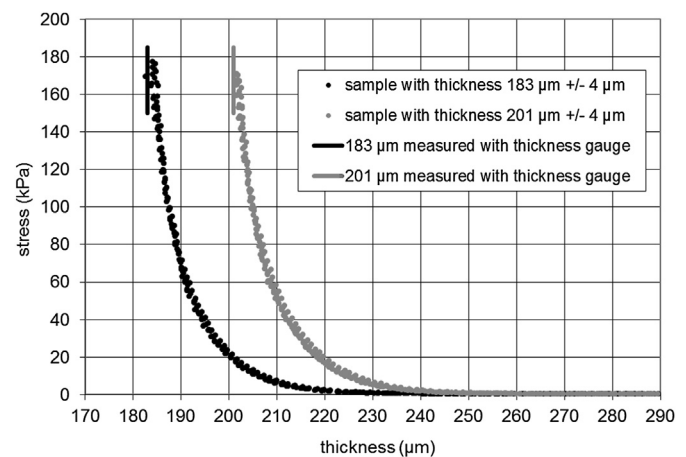

Fig. 12. Cyclic stress−strain curve of sample A (measured thickness: 183 μm ± 4 μm) and sample B (measured thickness: 201 μm ± 4 μm).

generation of two point clouds which are labeled by triangles and circles. The circles represent the basis weight and thickness data of samples which are taken from the side of the substrate with the strongest periodic oscillations in thickness and basis weight. In Figs. 5 and 10 this is the area with a value for the substrate width higher than 17 cm. The triangles represent the remaining data.

Both data clouds show a linear dependency between the basis weight and the thickness. There are two obvious regions in the substrate. In region 1 (circles) the average density ρ (defined by Eq.
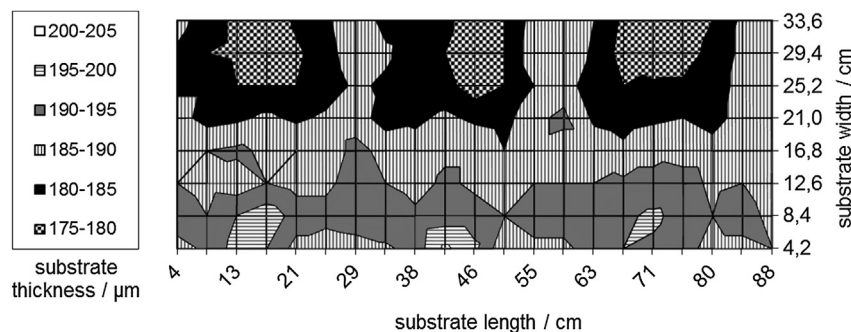

Fig. 10. Contour plot of substrate thickness (type: *s—i*) as a function of substrate length and width. The dark regions in the upper part of the diagram show the areas with lower thicknesses.
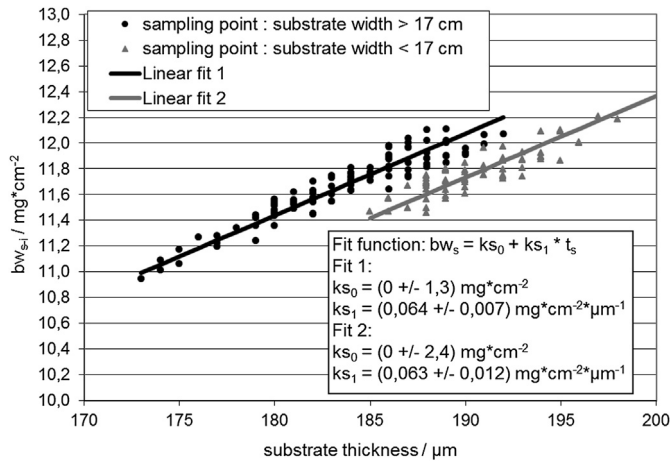
Fig. 13. Substrate basis weight as a function of substrate thickness. The two data point clouds are generated by the periodic structure in the substrate.

(11)) and the oscillations are higher than in region 2 (triangles) which has a lower average density and a lower scattering.

$$\rho = bw_s / t_s \qquad (11)$$

The coefficients of a linear function are fit for each region by a linear regression and are plotted in Fig. 13. Within the uncertainty the correlation between the basis weight and the thickness, expressed by the coefficient ks_1, are equal in both regions of the substrate. The coefficient ks_1 is required for the determination of the variance of the catalyst basis weight in Eq. (10).

According to Eq. (10), for the determination of the covariance between substrate basis weight and electrode basis weight a further parameter which describes the correlation between the electrode basis weight and the coating thickness is needed. In the next section it is explained how this parameter can be determined experimentally.

3.2. Determination of the coating thickness

To produce an electrode with a specific value of catalyst basis weight, the right adjustment of the knife height in the coating unit must be determined. A first approach in a laboratory experiment provides a rough value for the knife height. Unfortunately, the laboratory experiments are often not fully comparable with the pilot plant experiment. Therefore, the knife height has to be determined exactly by a pilot plant calibration. For this calibration the substrate is coated with the catalyst dispersion over a reduced coating width of approximately 15 cm in the middle of the substrate. During the experiment the coating thickness is changed after each 50 cm. The electrode basis weights of the coated areas are determined with the methods described in Section 2.2. The electrode basis weight as a function of the coating thickness, which is the difference between knife height and the mean of the substrate thickness, provides the data for the calibration curve shown in Fig. 14.

A linear function is fitted to the data points to determine the constants of the calibration curve. This provides the parameter ke_1, which describes the correlation between the electrode basis weight and the coating thickness needed for Eq. (10). The next section describes the substrate coating with catalyst dispersion.

3.3. Coating of catalyst dispersion on substrate s–i

The target value for the catalyst basis weight is 3.2 mg cm^{-2}, and the catalyst content in the solid phase of the dispersion is
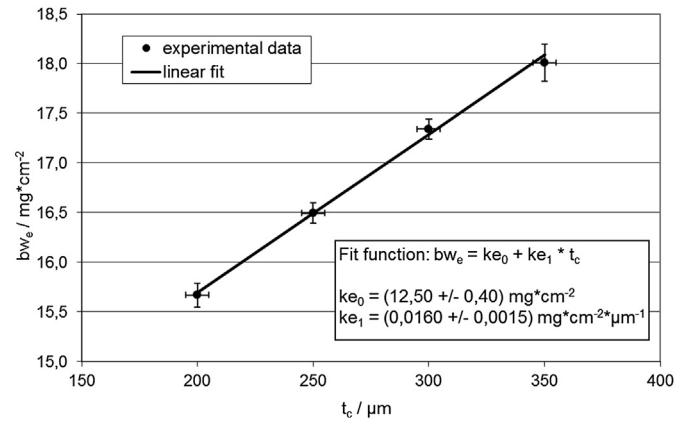

Fig. 14. Electrode basis weight as a function of coating thickness. The calibration curve is needed for the electrode production.

$\omega_{cat} = 0.504$. According to Eq. (4), the required electrode basis weight is 18 mg cm^{-2}, and by using the calibration curve the required coating thickness is 350 μm. After the coating the basis weight of one meter electrode is investigated. Fig. 15 shows the frequency distribution of the measured data. The Jarque–Bera test of the electrode basis weight provides a p-value of 26.1%. In contrast to the result of the Jarque–Bera test for the substrate basis weight a normal distribution cannot be ruled out.

Additionally, Fig. 16 shows the electrode basis weight as a function of electrode length and width. Of particular note are the low values for the basis weight (dark regions) at the electrode edges in combination with the high values (bright regions) in the middle of the electrode. This structure is not comparable with the observed structure in the substrate. Therefore, a homogeneous coating of the catalyst cannot be assumed.

In order to see this structure more clearly, the mean and the standard deviation over the electrode width as a function of electrode length and over the electrode length as a function of the width are calculated. Fig. 17 shows the results. In comparison to the basis weight of the substrate periodic structures are neither seen in the mean nor in the standard deviation (see Fig. 17A). In Fig. 17B a maximum in the electrode basis weight of 18.1 mg cm^{-2} is clearly visible in the middle of the electrode. At the edges of the electrode the basis weight decreases to a value of 17.7 mg cm^{-2}.
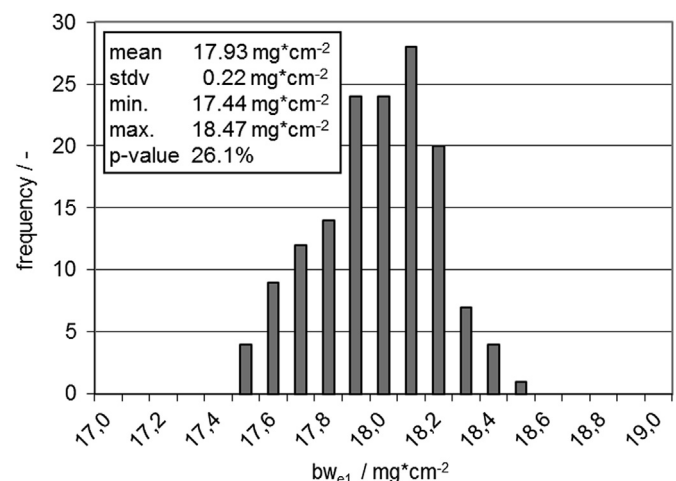

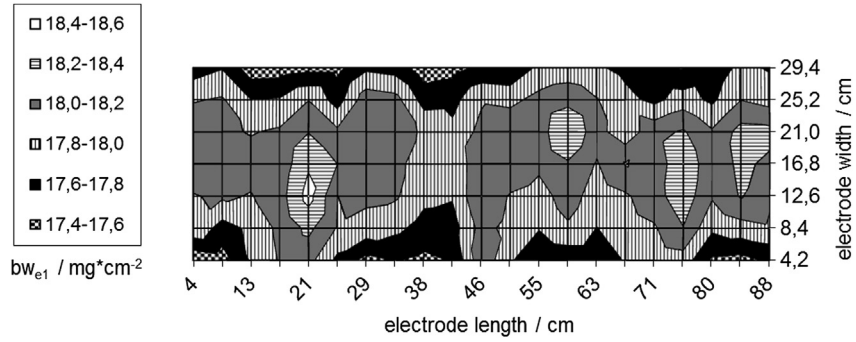**Fig. 15.** Frequency distribution of the electrode basis weight.

Fig. 16. Electrode basis weight as a function of electrode length and electrode width. The dark and bright regions show a new structure along the electrode length.

A deeper investigation into the source of this structure follows in Section 3.5. At this point all parameter values for the calculation of the mean and the variance of the catalyst basis weight are known. The next section is focused on the quantification of these parameters.

3.4. Determination of the mean and the variance of the catalyst basis weight

The presented experimental data from Section 3.1 up to Section 3.3 are listed below.

Properties of the used catalyst dispersion	
Catalyst content in the solid phase	$\omega_{cat} = 50.4\%$
Substrate properties (s−i)	
Basis weight	
Arithmetic average	$E(bw_s) = 11.72$ mg cm^{-2}
Standard deviation	$stdv(bw_s) = 0.24$ mg cm^{-2}
Thickness	
Arithmetic average	$t_s = 187$ μm
Standard deviation	$stdv(t_s) = 5$ μm
Linear basis weight − thickness correlation	$ks_1 = 0.064 \pm 0.007$ mg cm^{-2} μm^{-1}
Correlation between electrode basis weight and coating thickness	
$bw_e = ke_0 + ke_1 \times t_c$	$ke_0 = 12.50 \pm 0.40$ mg cm^{-2}
	$ke1 = 0.016 \pm 0.002$ mg cm^{-2} μm^{-1}
Electrode properties	
Basis weight	
Arithmetic average	$E(bw_{e1}) = 17.93$ mg cm^{-2}
Standard deviation	$stdv(bw_{e1}) = 0.22$ mg cm^{-2}

By using Eq. (4) the mean of the catalyst basis weight can be calculated.

$$E(bw_{cat}) = \omega_{cat} \times (E(bw_{e1}) - E(bw_s)) = 0.504 \times (17.93 - 11.72)$$
$$\text{mg cm}^{-2} = 3.13 \text{ mg cm}^{-2} \tag{12}$$

For the calculation of the variance Eq. (10) is used.

$$stdv(bw_{cat}) = sqrt(var(bw_{cat}))$$
$$= \omega_{cat} \times sqrt\left(stdv(bw_s)^2\right) + 2 \times ks_1 \times ke_1(stdv(t_s))^2$$
$$+ \left(stdv(bw_{e1})^2\right)$$
$$= \omega_{cat} \times sqrt(0.0576 + 0.0512 + 0.0484) \text{ mg cm}^{-2}$$
$$= 0.200 \text{ mg cm}^{-2} \tag{13}$$

According to Section 3, the target value for the catalyst basis weight is 3.2 mg cm^{-2} and for the standard deviation 0.05 mg cm^{-2}. The evaluation of the data provides that the desired value for the catalyst basis weight can be adjusted within the uncertainty, but the target value for the standard deviation is approximately four times smaller than the experimental value. To understand the source of the catalyst basis weight scattering, the different contributions to the standard deviation are investigated in the next section.

3.5. Influences on the variance of the catalyst basis weight

This section is focused on the different contributions to the variance of the catalyst basis weight according to Section 2.3. In Eq. (13) are three inputs which have to be taken into account for the determination of this variance.

1. The first summand in the brackets of the root of Eq. (13) describes the scattering of the substrate basis weight. This is a
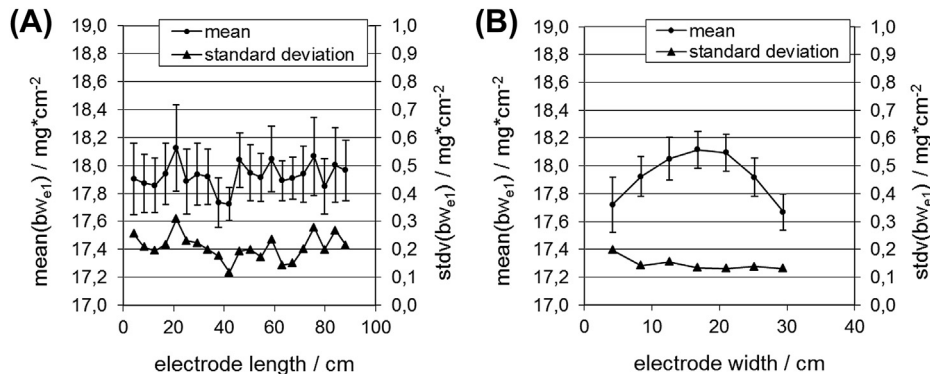

Fig. 17. Mean and standard deviation of electrode basis weight. A: Mean and standard deviation over the width as a function of length. B: Mean and standard deviation over the length as a function of width.

method-inherent contribution because of the calculation of the difference in Eq. (4).

2. The second summand depends on the scattering in the substrate thickness which influences the coating thickness and therefore the catalyst basis weight (see Section 2.1.3). Furthermore, this summand depends on the correlation between the electrode basis weight and the coating thickness because of the constant ke_1. This parameter contains also the information about the penetration of the catalyst dispersion in the substrate.

3. The third summand describes the scattering of the electrode basis weight. Three cases have to be distinguished:
   a. The basis weight scattering of the coated layer is negligible. In this case the basis weight scattering of the electrode and the substrate are equal ($\text{stdv}(bw_e) = \text{stdv}(bw_s)$). Electrode basis weight structures are equal to the substrate basis weight structures.
   b. Processes during the coating or the subsequent drying lead to an additional scattering effect in the coated layer which generates an additional contribution to the scattering in the substrate basis weight ($\text{stdv}(bw_e) > \text{stdv}(bw_s)$). Electrode basis weight structures are added to the substrate basis weight structures.
   c. The coated layer is smoothing the basis weight of the substrate. Thin areas are coated with excess of dispersion while thick areas are coated with little dispersion. In the case of a positive correlation between the substrate basis weight and the thickness the scattering of the substrate basis weight will be higher than for the electrode ($\text{stdv}(bw_e) < \text{stdv}(bw_s)$). Electrode basis weight structures are added to the substrate basis weight structures.

The substrate properties are responsible for inputs 1 and 2 and can only be changed by choosing another substrate or developing improved substrate production methods.

The cases 3a, 3b, and 3c are influenced by the coating and drying process. They can be distinguished by a direct comparison of the measured standard deviations of the substrate and electrode. Additionally, the structure in the basis weight of the substrate and the electrode provides important hints to improve the homogeneity of the catalyst basis weight. The following section describes the investigation of the produced electrodes by using these rough differentiation criteria.

3.5.1. Influence of the coating machine

The standard deviation of the substrate basis weight (0.24 mg cm^{-2}, see Fig. 4) is very similar to the standard deviation of the electrode basis weight (0.22 mg cm^{-2}, see Fig. 15), but no periodic structure is present in the substrate basis weight (see Fig. 5). Remarkably, a new structure with a maximum is visible in the electrode basis weight (see Fig. 17B). This is an indication for an additional effect during the coating process. This can be classified as case 3b.

The most probable cause for this shape is the coating knife. Therefore, the knife edge is analyzed by a laser measurement device. It is found that the knife blade has a curvature so that the height in the middle of the knife is approximately 60 μm higher than at the edges.

The knife blade was ground, and measured again. Fig. 18 shows the shape of the knife blade before and after the grinding. It is clearly visible that the maximum variation of the height along the knife blade can be reduced from 60 μm to 20 μm by regrinding.

Fig. 18 also shows the range in the middle of the knife which is used for the calibration, described in Section 3.2. For the further discussion it is important to note that in relation to the coating
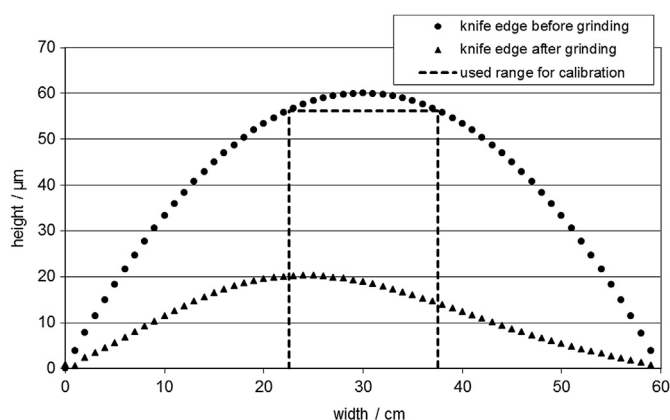
Fig. 18. Course of the knife height along the blade: The circles show the course of the height before the grinding the triangles the course after the grinding. The labeled range in the middle shows the area used for the calibration.

process a knife height of zero means the edges of the knife are on the cylinder coating roll. In this case there is still a distance of 60 μm in the middle of the knife. After the grinding the knife height in the middle of the blade is approximately 40 μm smaller. Consequently, in case of a new coating experiment with the same adjustments like before a lower coating basis weight has to be expected.

To proof whether or not the shape of the knife is responsible for the shape in the electrode basis weight, a piece of substrate is coated again with the same adjustments as before. Fig. 19 shows the frequency distribution of the measured electrode basis weight. In comparison to the situation before the knife grinding the mean of the distribution is smaller and the standard deviation is similar. The Jarque–Bera test provides a p-value of 37.3% in comparison to 26.1% (see Fig. 15). With respect to this test the probability for a normal distribution is higher than before the knife regrinding.

Fig. 20B clearly shows that the maximum of the electrode basis weight in the middle of the electrode is removed after the knife was reprocessed.

In summary one can say that the reduction of the curvature in the knife blade leads to a better homogeneity transverse to the electrode length. The probability for a normal distribution is increased, but the impact of the knife grinding on the standard deviation of the electrode basis weight is very low. The optimized knife is not able to avoid a more or less periodic increase of the standard deviation from approximately 0.15 mg cm^{-2} to
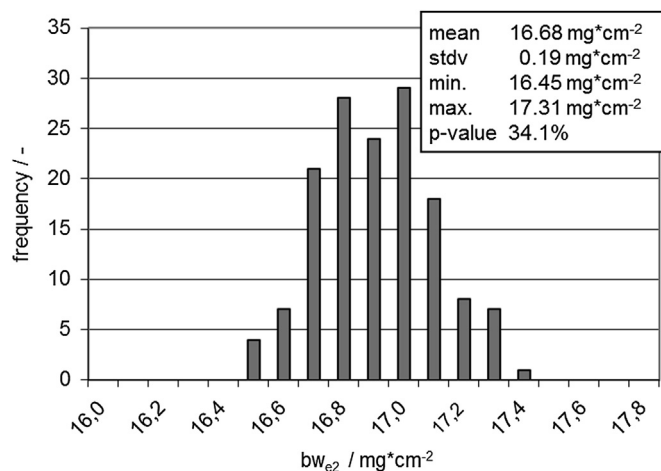
Fig. 19. Frequency distribution of the electrode basis weight after the knife grinding.
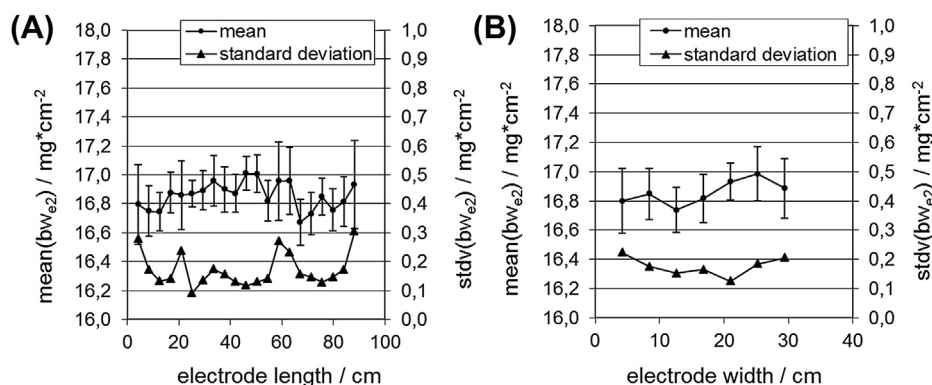
Fig. 20. Mean and standard deviation of electrode basis weight. A: Mean and standard deviation over the width as a function of length. B: Mean and standard deviation over the length as a function of width. In comparison to Fig. 17B the maximum in the mean is disappeared after the regrinding of the knife.

0.25 mg cm^{-2} along the electrode length (see Fig. 20A). It is unlikely that the knife is the source of these peaks. More likely is that these peaks are induced by the substrate. Therefore, the substrate influence on the standard deviation of the catalyst basis weight is discussed in the next section.

3.5.2. Influence of the substrate

After the regrinding of the knife the standard deviation of the substrate basis weight (0.24 mg cm^{-2}, see Fig. 4) is higher in comparison to the standard deviation of the electrode basis weight (0.19 mg cm^{-2}, see Fig. 19). Fig. 21 shows the centered frequency distributions of the substrate and electrode basis weight.

The diagram clearly shows lower scattering of the electrode basis weight. The tail of the distribution for low substrate basis weight values is removed. These low values can be attributed to the low basis weight areas of the periodic structure in Section 3.1.1. Consequently, it can be assumed that the inhomogeneity of the substrate basis weight is partially compensated by the catalyst dispersion which can be classified as case 3c.

To compare the structure of the substrate basis weight and the electrode basis weight, the substrate basis weight data is plotted as a surface plot in Fig. 22. The basis weight of the electrode produced with the grinded knife is shown as a contour plot in Fig. 23. The cyclical pattern of the substrate basis weight shows minima with distances of approximately 25 cm and values of approximately 11.2 mg cm^{-2} (see also Section 3.1.1). The basis weight of the electrode has periodic maxima with a distance of approximately

25 cm and values of 17.0 mg cm^{-2}–17.3 mg cm^{-2} (see Fig. 23). The periodic structure is not visible in the electrode thickness data, presented in Fig. 24.

A conclusion of these considerations is that the sloped surface and the minima of the substrate thickness, presented in Fig. 11, are filled-up with catalyst dispersion during the coating. This results in an inhomogeneous catalyst distribution as indicated by following considerations.

Most of the interfering periodic structures are at the edges and not in the middle of the electrode and substrate. Therefore, the basis weight data in the middle of the substrate and electrode width are interpreted as a reference. Fig. 6B shows that the standard deviation of the substrate basis weight has a minimum at a substrate width of 17 cm. At this position the mean is 11.82 mg cm^{-2}, and the standard deviation is 0.11 mg cm^{-2}. At the same position the mean for the substrate thickness is 189 μm, and the standard deviation is 2 μm. According to Fig. 20, the mean for the electrode basis weight at this position is 16.82 mg cm^{-2}, and the standard deviation is 0.17 mg cm^{-2}. Additionally, with the data presented in Fig. 24 the thickness in the middle of the electrode can be determined. The mean is 243 μm and the standard deviation is 4 μm.

With this data the coated basis weight per thickness can be calculated.

$$bw_{cat}/t_{cat} = (bw_e - bw_s) \times (t_{cat})^{-1}$$
$$= (16.82 - 11.82) \times (243 - 189)^{-1} \, \text{mg cm}^{-2} \, \mu\text{m}^{-1}$$
$$= 0.0926 \, \text{mg cm}^{-2} \, \mu\text{m}^{-1}$$
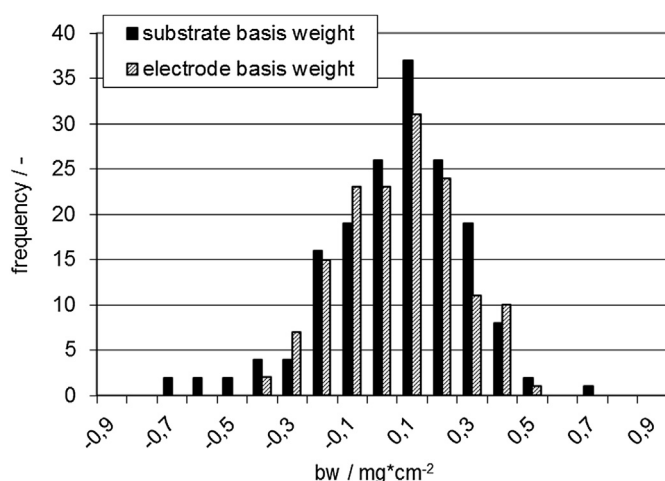
$$(14)$$

Fig. 21. Centered frequency distributions of the substrate and electrode basis weight.
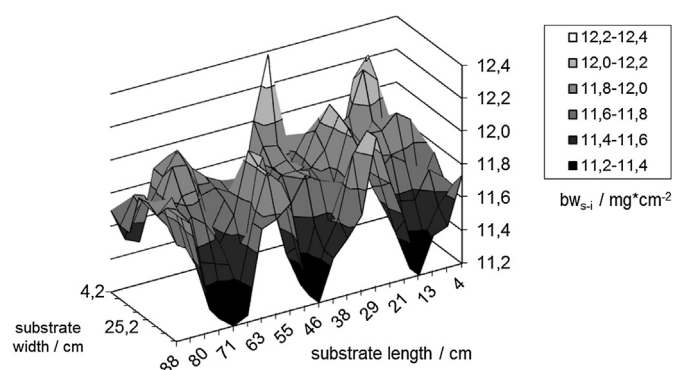

Fig. 22. Surface plot of the substrate basis weight (type: s–i) as a function of substrate length and width. Fig. 5 represents the same data as a contour plot.
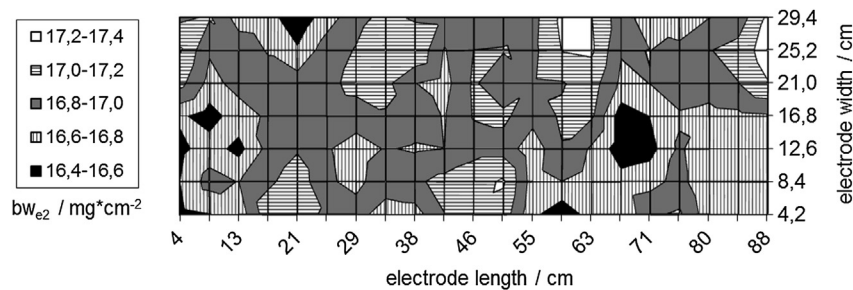
Fig. 23. Electrode basis weight as a function of electrode length and electrode width. Because of the knife grinding the maximum in the middle of the electrode is disappeared.
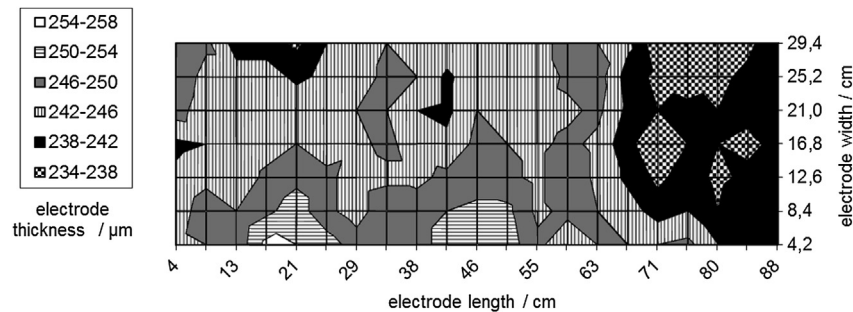

Fig. 24. Electrode thickness as a function of electrode length and electrode width.

Assuming that the regions of the substrate with the low basis weight of approximately 11.1 mg cm^{-2} and a thickness of approximately 175 μm are filled up to a thickness of 243 μm, it has to be expected that the coated basis weight is:

$$bw_{coat} = (243 - 175) \times 0.0926 \text{ mg cm}^{-2} = 6.30 \text{ mg cm}^{-2} \qquad (15)$$

The expected electrode basis weight is calculated as follows:

$$bw_{e\_expected} = 11.1 \text{ mg cm}^{-2} + 6.30 \text{ mg cm}^{-2} = 17.4 \text{ mg cm}^{-2} \ (16)$$

When the regions of the substrate out of the minima, with a basis weight of 11.8 mg cm^{-2} and a thickness of 193 μm, are filled up to a thickness of 243 μm the expected coated basis weight is:

$$bw_{coat} = (243 - 193) \times 0.0926 \text{ mg cm}^{-2} = 4.63 \text{ mg cm}^{-2} \qquad (17)$$

The expected electrode basis weight is calculated as follows:

$$bw_{e\_expected} = 11.8 \text{ mg cm}^{-2} + 4.63 \text{ mg cm}^{-2} = 16.4 \text{ mg cm}^{-2} \ (18)$$

According to Fig. 19, the minimum of the measured electrode basis weight is 16.45 mg cm^{-2}, and the maximum is 17.31 mg cm^{-2}. These values are very similar to the calculated data. This rough calculation demonstrates that the observed scattering in the electrode basis weight can be explained by a smoothing effect induced by the periodic structure in the substrate.

To summarize this section, it can be said that an imprecise produced coating knife is identified as the initiator for a parabolic shape in the produced electrode basis weight along the electrode length. The curvature of the knife is reduced and the parabolic shape cannot be measured again after a new electrode production.

With the reprocessed coating knife it is possible to detect a periodic structure in the electrode basis weight which is attributed to the inhomogeneity of the substrate thickness distribution. The estimated variation in the catalyst basis weight caused by this thickness inhomogeneity is too high for the production of highly efficient electrodes for direct methanol fuel cells. For the further improvement of electrode production processes substrates with lower variances in basis weight and thickness are needed.

4. Conclusions

The presented work is focused on the investigation of the statistical variance of the catalyst basis weight of continuously manufactured electrodes for direct methanol fuel cells. Statistical considerations of a knife coating process provide the dependencies between the variance of the catalyst basis weight, substrate basis weight, substrate thickness, and the covariance between electrode and substrate basis weight. The derived equations allow the quantification of the different contributions to the variance of the catalyst basis weight.

The major result of the investigations is that different effects influence the catalyst basis weight distribution of the manufactured electrodes. The basis weight and thickness analyses of the substrate used indicate that periodic structures create a large contribution to the variances of the basis weight and thickness. Furthermore, the basis weight and thickness investigations of the manufactured electrodes clearly show that a construction fault of the coating knife used is responsible for a gradient in the coated catalyst layer. This structure can be removed by regrinding the knife, but the impact on the homogeneity of the electrode basis weight is rather low. After removing the gradient, a new periodic structure in the produced electrodes is visible. It can be demonstrated that this periodic structure is generated by the structure in the substrate used. The thickness minima in the substrate are filled with catalyst dispersion, and because of the high density of the catalyst the substrate basis weight minima are transformed into electrode basis weight maxima by the knife coating process. This filling process is responsible for the observed large standard deviation of the electrode basis weight of 0.19 mg cm^{-2}. Thus, the homogeneity of the manufactured electrodes is limited by the homogeneity of the substrate used. In order to meet the targets for

the variance of the catalyst basis weight, another substrate with lower variances of basis weight and thickness is required. The alternative to this approach is to use another coating technique for the electrode production.

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List of symbols

A: sample area
m_s: mass of substrate sample
m_e: mass of electrode sample
bw_s: substrate basis weight
bw_e: electrode basis weight
bw_{cat}: catalyst basis weight
bw_{coat}: coated basis weight
t_s: substrate thickness
t_{cat}: thickness of catalyst layer
kh: knife height
t_c: coating thickness
$E(x)$: expectation value of random variable x
$var(x)$: variance of random variable x
$cov(x,y)$: covariance between two random variables x and y
ρ: average density
ω_{cat}: solid content of catalyst in the solid phase of the dispersion
ks_0: constant offset for linear substrate basis weight function
ks_1: slope for linear substrate basis weight function
ke_0: constant offset for linear electrode basis weight function
ke_1: slope for linear electrode basis weight function
wt: wet film thickness
$bw_{e\_expected}$: expected electrode basis weight